Assessment of PotentiallyToxic ElementsPollution ~~by Heavy Metals~~ in Surface Sediments at Wadi Al-Wala, Jordan

Abstract

Concentrations of Cd, Fe, Cu, Mn, Pb, and Zn in sediment samples from Wadi Al-Wala were determined ~~in order~~ to assess ~~the level of~~ theircontaminationlevel. Sixteen sediment samples were collected ~~during the period from 2016~~from the studyareaand subjected to chemical analysis.The extremelyhigh~~est~~ concentrations of Zn,Cd~~, Cu~~and ~~Cd~~ Mn weredetected to have originated mainly from anthropogenic sources such as discharge of agricultural material~~s~~ residuals,~~and~~ industrial waste and gasoline additives used in industries and automobiles.~~the weathering of surrounding rock formations.~~The contamination assessments of the surface sediment samples from the study area were carried out using pollution indicators such as enrichment factor (EF), pollution load index (PLI), and geo-accumulation index (Igeo).~~Sediment contamination assessment was carried out using the pollution indicators such as enrichment factor (EF), pollution load index (PLI), and geo-accumulation index (Igeo).~~The~~Results of~~ Igeo ~~analyses~~ assessmentof Wadi Al-Wala sediments ~~proved~~ indicatethat concentrations of ~~Mn~~Fe,~~, Cu,~~ Pb, and ~~Fe~~ Cuare within safe leveland thattheywere notimpacted ~~these elements are practically unchanged~~by anthropogenic influences, ~~while the~~ unlike like ~~concentration of~~ Zn,Cd and ~~Cd~~ Mnwhichexceeded their average concentration values.The result of EF showed high concentrations of Zn, Cdand Mnin the study area.Conversely,PLI analysis ~~proved~~established that ~~Wadi Al Wala is moving towards a probable~~the study area isbeing environmentally~~pollution~~ polluted with extremehigh concentrations of ~~regard to heavy metals (~~Zn, Cd, and ~~Cd~~Mn~~),~~ ~~while.~~.~~The results of EF showed high concentrations of Zn, Cu and Cd in the study area.~~ Correlation coefficients analysis carried outshowed varying relationship between the different parameters ~~depending~~indicative of the input sources of thepotentially toxic elements in the study area. ~~on the input sources of each metal~~Regular environmentalpollution monitoringand mitigationinclusiveof management and control of ~~. In order to protect the sediments from further contamination, monitoring and management of the heavy metal~~ anthropogenic discharges ~~is suggested~~arerecommendedfor Wadi Al-Walaarea.

Key words: Wadi Al-Wala, Sediments, ~~Heavy metals~~PotentiallyToxic, ElementsPollution ~~Assessment~~, Jordan~~.~~

1. Introduction

Environmental pollution is a problem in modern societies. Out of the various kinds of pollution, high contamination of aquatic systems with potentially toxic ~~heavy metals~~elements is of major concern since these elements are not biodegradable and their elevated uptake by crops may also affect food quality and safety. ~~Heavy metals~~Potentially toxic elements enter the~~se~~ aquatic systems mainly through natural inputs such as weathering, ~~and~~ erosion of rocks and runoffand anthropogenic sources ~~including~~ such asurban, industrial and agricultural activities, ~~terrestrial runoff~~and sewage disposal **[1]**.Potentially toxic elements~~Heavy metals~~ discharged into aquatic systems may be immobilized within stream sediments by ~~main~~ processes such ~~us~~ asadsorption, flocculation and co-precipitation. Therefore, sediments in aquatic environments serve as a pool that can retain metals or release metals to the water column by various processes of remobilization **[2, 3, 4]**. Several processes lead to the association of potentially toxic elements~~heavy metals~~ with solid phases, such as direct absorption by fine-grained inorganic particles of clays; adsorption of hydrous ferric and manganic oxides which may in turn be associated with clays~~;~~by adsorption on or forming ~~complication~~ complexwith natural organic substances, or ~~associated~~ associationwith inorganic particles, or by~~and~~ direct precipitation as new solid phases [**5**]. Numerous studies have ~~demonstrated~~ establishedthat the concentrations of metals in sediments can be used as sensitive indicators of contaminants in aquatic systems **[6,7,8,9,10]**. Many approaches have been applied in order to assess the severity of sediment contamination and to understand the natural and anthropogenic inputs in ~~the~~ river systems.

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The main ~~objective~~ aimof this study ~~was~~ istocharacteriz~~eationof selected heavy metals~~potentially toxicelements concentration level and spatialdistribution of ~~(~~Copper, Zinc, Cadmium, Manganese, Iron, Arsenic and Lead~~)~~ in the surface~~s~~ sediments ~~for distribution and concentrations in sediments from~~in Wadi Al-Wala areain Jordan. To achieve the abovementioned aim, ~~Also, it aims to~~ various assessmentsof potentially toxic elements ~~sediments~~pollution potentiality ~~by~~ will be carried out ~~heavy metal~~ using Geo-accumulation (Igeo), Pollution Load I~~i~~ndex (PLI) and Enrichment Factor (EF) and Pearson's correlation coefficients for different parameterswillbe performedaccordingly. In turn, usingthese ~~This~~ assessments,thepotentially toxic elementspollution levelsand sources of pollution will be determinedand the possibleenvironmental solutionsto both manage andcontainthe pollutionsources.~~will help in providing a better perspective about the contamination amount and sources in the study area, which in turn will help in understanding the mechanisms driving and controlling this contamination. This study also aims to assess the various sources of contamination to have a prospect regarding the possible prevention of this contamination.~~

2. Study Area

2.1 Geographical Location

The study area is Wadi Al-Walaandit is located in the middle part of Jordan,andit~~Wadi Al-Wala~~lies between latitudes (30º 20' and 31º50'N and between longitudes (35°12' E and 36°38'E). The study area~~, it~~ occupies an area of about 2,050 km^2 (Fig. 1). The studyarea is ~~a~~ part of Al-Wala basin in the middle parts of Jordanwith~~; the~~total area of ~~the basin is~~ 1,900 km^2. The basin has a flat topography in the east and steep slopes in the west. Altitude of the study area varies from 321 m below sea level at the eastern shoreline of the Dead Sea (lowest point on earth) to 997 m in the eastern parts of the study area. The basin is dominated by an arid Mediterranean climate with relatively cold winters and hot summers. The mean monthly air temperature ranges from 6˚C in January andup to 22˚C in August, with a mean annual air temperature of 15~~.0~~˚Cw~~.~~ ~~W~~ith exception to northwestern parts. The mean annual rainfall is 100 - 200 mm~~, occurring mainly during winter season (October-April).~~. The mean annual potential evaporation ranges from 1,600 mm in the western parts to 2,000 mm in the east and 2,200 mm at the outlet near the Dead Sea. In terms of land use, about 47% of the basin is used as open range-lands~~rangelands~~. Agricultural activity is also taking place in the basin where rain-fed cultivation of wheat and barley is practiced in 38% of the basin. Irrigated areas form 3% of the total area of the basin, while 7% of the basin is urban [**11].**

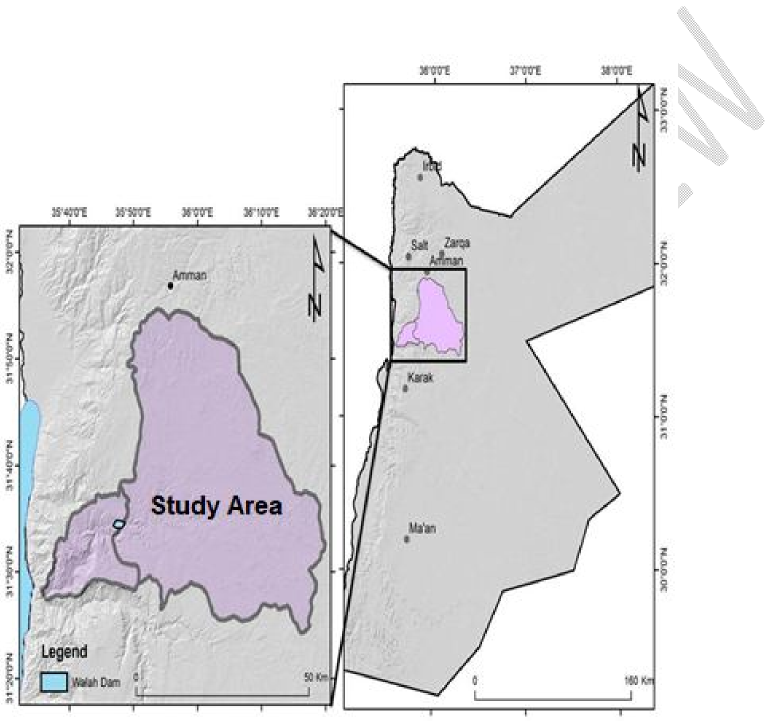

Fig. 1: Location map of the study area

2.2 Geological Setting

The area study iscovered by upper C~~c~~retaceous~~group~~ Belqa and Ajlun Group, respectively(Fig. 2). The groups are mainly dominated by C~~c~~retaceous carbonate rocks that outcrop in most of the study area [**12].** The oldest rock that outcrops in the study area is the upper Wadi ~~as~~ Sir Limestone (WSL) F~~f~~ormation, deposited in an agitated marine environment~~, from~~in the Turonian~~ age~~. The lower part is composed of marl, marly limestone, coquina, m~~M~~icrite, sand and dolomicrite with ~~C~~chert nodules ~~that has an~~with average thickness of 62 m. The upper part is composed of limestone, dolomitic limestone and fossiliferous limestone with an average thickness of about 4.5 m [**12].**

A~~n a~~brupt change in sedimentation which resulted~~resulting~~ from ~~an~~ extensive Coniacian marine transgression marked~~s~~the base of Belqa G~~g~~roup ~~where a~~which is madepredominantly ofchalky unit of Wadi Umm Ghudran(WG) F~~f~~ormation of Coniacian-Santonian age that overlies Ajlun

G~~g~~roup. This formation consists of Mujib Chalk, brecciated dolomitic limestone, and Dhiban Chalk with fish teeth out cropping all over the basin area. The formations of Belqa group include Al Hisa Phoshorite F~~f~~ormation (AHP)which is~~, (~~of Campanianageand it~~), which ~~consists of dark grayish c~~C~~hert, marly limestone and phosphate, and thenthe Muwaqqar Chalk Marl F~~f~~ormation (MCM) of ~~(~~Maastrichtian agecomposed~~), which consists~~of marl and chalk with chalky and micritic limestone concretions. ~~Also ~~Nextis ~~it includes ~~Madaba Calcareous Breccia (MCB) of ~~(~~Eocene age~~),~~ which consists of brecciated and partly conglomeratic clasts of phosphate, limestone, che~~a~~rt and chalk in a mudstone matrix located on hills, slopes and along some Wadiin Madaba area.

Additionaly,~~The geology of the study area has some unique formations that include ~~basaltic flows of Pleistocene agecomposedof~~, as ~~volcanic tuffs are found restricted to the upper courses of Wadi Al Haidan. Lastly, Quaternary Superficial Deposits (Pleistocene age) of Fluviatile and Lacustrine Gravels~~(Pl)~~cover most of the wades of the basin, particularly in the east. Aridic soils are dominating the lower rainfall zones, while dark brown Mediterranean soils are dominating the high rainfall zones.

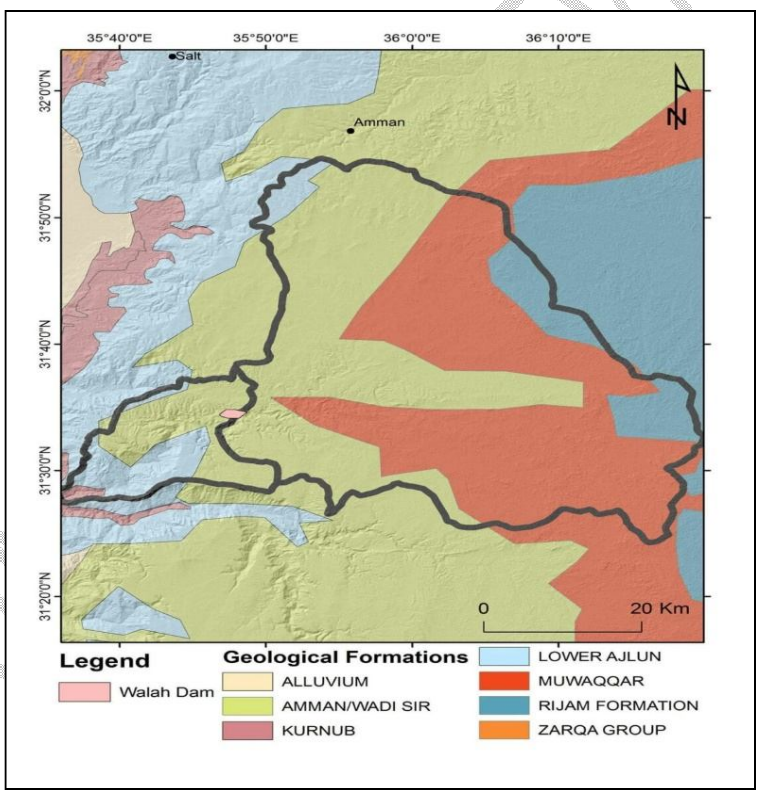

Fig. 2: Geological Map of the study area

3. Sampling and Analytical Techniques

Sixteen sStream sediment samples were gathered collectedat depths of 0-20 cmalong the main valley of Wadi Al WalaWadi Al-Wala. Samples were collected at depths of 0-20 cm during. The sampling of theSamples were collected in a manner to cover the whole stream sedimentswasdesignedto coverthe entire in the study area (Fig. 3). Large stones and debris were first removed. Then, sediment samples were air-dried and put in stainless steel sieve to remove very large particles to have a homogenous sample. Afterward, samples were transferred to labeled, pre-washed, polyethylene bags to beand transported to the laboratory for further sample preparation and analysis.

3.1 Extraction

The samples were prepared and then were dried in the anoven at 55°C for 2 hours. All Thedried samples were sievedto;particles <63 µm (0.05-mm) sizeswhich in size were chosen to be analyzed as this size is has beenproven to be the best sedimentsize for analysis for arid and semi-arid regions [**13]**.

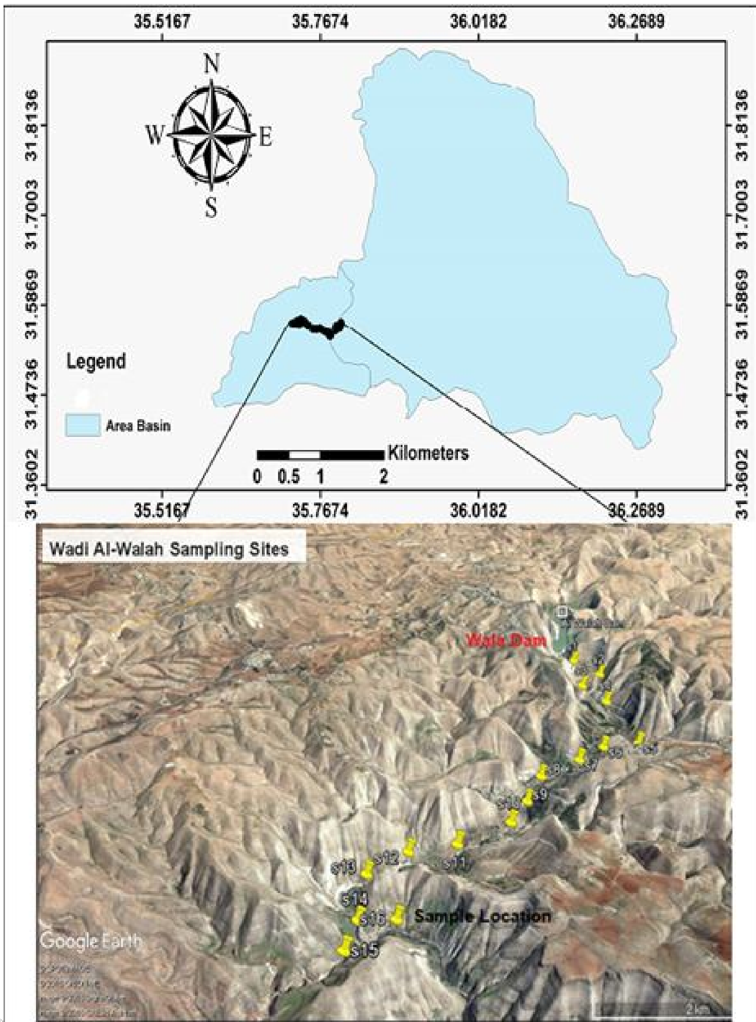

Fig. 3: Sample location map

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The extraction method is used in pollution studies to determine the ~~heavy metal~~potentially toxic element~~contents~~ concentrationsand the best extraction results were obtained ~~with~~ usingAmmonium-Acetate-EDTA Extractionmethod. 20 g~~m.~~ air-driedy~~y~~ soil samples were placed in a 300 ml Erlenmeyer flask, ~~with~~ and ~~adding~~ 100 ml extracting solutionwas then addedand~~.~~the content~~. Then, it~~ was shaken mechanically for 30 minutes. Thereafter,~~After shaking,~~ the suspension materials were filtered and the filtrate was collected into a polyethylene flask.

3.2 Percentage of Carbonate

To determine the carbonate (CO_3^{2-}) content of the samples, study using titration method for wasused[14]. The ThesSamples were preparationed by millinginto powderand then using (2.5 gm.)eachwas taken from from each of the powdered samples and then 100 ml of 1.N. of HCl were added to the sample while keeping the beaker undisturbed for about 20 minutes. Thereafter,, after that, iteachcontent was stirred with a glass rod. Than aAfter 20 minutes, the eachsolution was filtered and the clear solution was collected in a new beaker. ThereafterAfter that,Ttitration of the blank was carried out byusing 20 ml of 1.N. HCl were taken by witha pipette, and then it was placed put it in a conical volumetric flaskinto which, then,4 or 5 drops of bromophenol blue indicator were addeduntil, and then, the solution turned to yellow color. At the end point of the titrationprocess, the color of the solution in the conical volumetric flask turned blue. At this step, the reading on the burette and the amount of NaOH used in the solution were recorded. This procedure was repeated three timesfor another blank titration three times and the average blank valueswas werecalculated. Titration of the samples from the studyareawasdone , using 20 ml of the eachof the sample solution from the first step previouslywere taken and thenput it waspouredinto the conical volumetric flask. Then, it was titrated with NaOH in the burette, with the addition of 4 or 5 drops of the bromophenol blue indicator.

At the end point of the titration, the color of the eachof thesample solution in the conical volumetric flask turned blue. At this step, the reading on the volumetric flask (burette) and the amount of NaOH used in the sample solution have beenwere notedand recordedas . This is the test of titration value. Theeis procedure for sample solution titration wasrepeated three times and the average test value was wascalculatedto getcarbonatepercentage as given in equation 1 below:.

Carbonate percent = 10 * (Blank value – Test value) ……………. equation 1

3.3 pPercent of Organic Matter (OM)

The percentage of organic matter (OM) were determine by using Ashing method (Lose On Ignition [15]. The Procedure isas follows:

i. 1 Clean a dried crucible at 105°C for 2 hours, cool, have been weighted and labeled it.

2 ii. Place2g of sample placed in the crucible andthen weigh sample and crucibleweighted.
3 iii. Heatsample insidecCrucibles placed with sample in muffle furnace at 500°C for two hours.
4 iv. Weigh cooledThe crucible and samples are weightedafter heating.
5 v. The amount of Organic Matter(OM) is calculated by subtracted the weight in step (4) from the weight in step (2). Combustion at 550° C converts Organic Matter (OM) to CO^2 according to the reaction: $CH_2O + O_2 \rightarrow CO_2 + H_2O$.

%OM = (weight sample before Ashing-weight sample after Ashing) / (weight sample before Ashing) * 100…………………………………………………………equation 2

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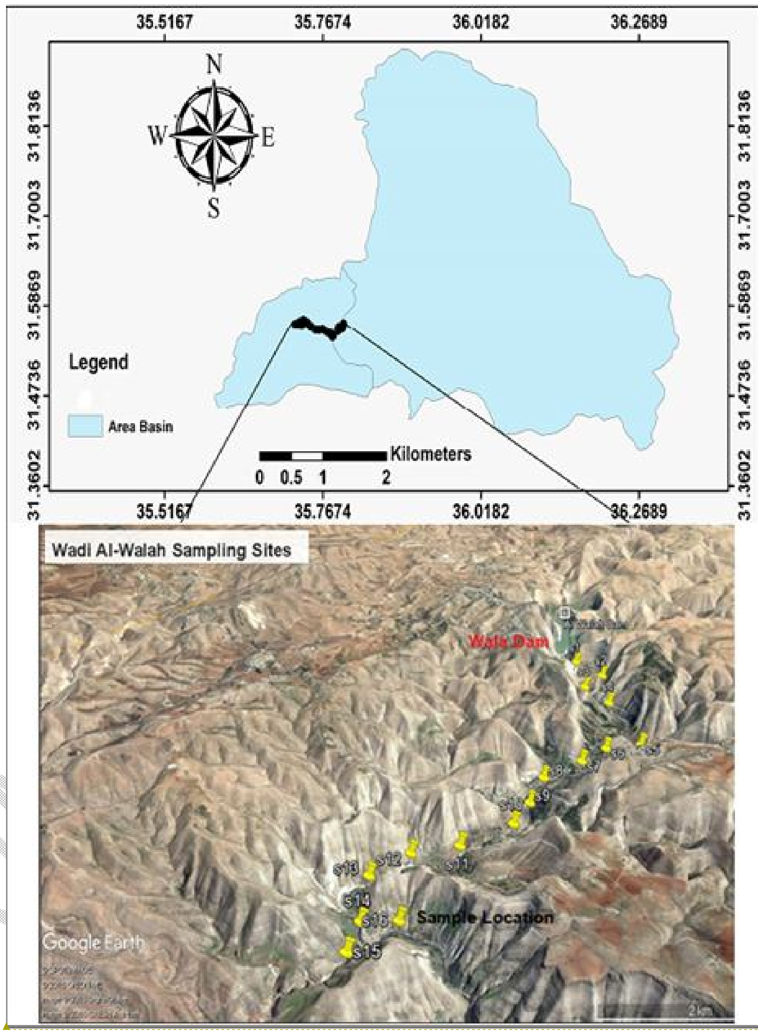
All the samples ~~study~~ were prepared~~ration~~ in the Laboratory of the Faculty of Earth and Environmental Sciences in Jordan University. The ~~heavy metals~~ potentially toxic elements analysis was done using Atomic Absorption Spectrophotometer ~~at~~ in Jordan University Laboratory. The result of the chemical analysis of the ~~studied~~ samples from the study area is ~~listed~~ presented in Table 1.



~~Fig. 3: sample location map~~

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Table 1: Result of the chemical analysis of the samples from the study area ~~Concentrations of Heavy Metals (Mg/l), CO_3 (WT%) and percent of organic matter (OM) for the Studied Samples~~

Sample No.	Cd	Fe	Zn	Cu	Pb	Mn	Wt % CO_3	% OM
	Mg/l							
1	0.404	7.25	4.092	0.744	0.203	12.592	50	0.541
2	0.446	7.35	1.248	0.087	0.291	15.768	60	0.806
3	0.833	3.05	3.194	0.211	0.459	22.142	20	0.612
4	0.606	8.147	9.316	0.2435	0.128	6.911	25	0.501
5	0.310	6.91	8.681	0.587	0.152	35.649	20	0.503
6	0.167	4.856	2.792	0.089	0.703	4.309	23	0.634
7	0.127	31.483	1.311	0.854	0.168	34.105	57	0.591
8	0.114	3.891	0.696	0.124	0.144	33.816	38	0.699
9	0.064	3.386	0.229	0.023	1.097	21.325	27	0.739
10	0.123	3.26	0.264	0.042	0.209	30.587	16	0.787
11	0.182	3.72	0.699	0.057	0.199	14.854	48	0.345
12	0.166	4.718	1.445	0.067	0.198	25.045	32	0.485
13	0.089	2.335	1.345	0.075	0.211	19.234	45	0.510
14	0.348	6.07	4.326	0.113	0.205	20.741	47	0.512
15	0.084	2.85	0.240	0.078	0.229	26.252	54	0.464
16	0.093	1.65	0.441	0.073	0.207	9.668	55	0.407
maximum	0.833	31.483	9.316	0.854	1.097	35.649	60	0.806
minimum	0.064	1.65	0.229	0.023	0.128	4.309	16	0.345
Average	0.260	6.308	2.520	0.217	0.300	20.812	38.563	0.571

4. Sediment Contamination Assessment

The contamination assessmentsof the surface sedimentsamplesfrom the study areawerecarried out using pollution indicators such as enrichment factor (EF), pollution load index (PLI), and geo-accumulation index (Igeo)~~To determine the level of heavy metals contamination in the surface sediments samples for the study area, there is many calculation methods have been proposed. These method is Enrichment Factor (EF), Pollution load index and Geoaccumulation index (Igeo)~~**[16,17].** The Enrichment factor (EF) was used to compare the metals originating from anthropogenic activities to those of geogenic natural origins, and to determine the degree of contamination and the possible anthropogenic impacts on the sediments of Wadi Al-Wala area. The EF analysis was first presented by Simex**[18]** to evaluate trace element concentration as follows in equation 3:

EF = (M/Fe) sample/ (M/Fe) background …………………………..equation 3

Where, M/Fe sample is the ratio of metal and Fe concentration in the sample, M/Fe background is the ratio of metal and Fe concentration of a background (The geochemical normalization of ~~heavy metal~~potentially toxic element data was employed for conservative elements such as Fe, Al and Si. According toSchiff and Mucha **[19 and 20]** ~~**(2003)**~~**,** Fe was used to normalize ~~heavy metal~~potentially toxic element contaminants. In this study, Fe was used as a conservative tracer to differentiate natural components from anthropogenic ones. The background concentrations of the potentially toxic element~~heavy metal~~ study ~~are~~ were taken fromTurekian and Wedepohl [**21].** The classification of pollution degree based on the enrichment ratio methodology was divided into a five-category system [**22]; If** (EF < 2), this implies a depletion to minimal enrichment suggestive of no or minimal pollution. If EF is within the range of 2–5, this indicates a moderate enrichment, suggestive of a moderate pollution. If EF is within the range of 5–20, it means a significant enrichment, suggestive of a significant pollution. If EF is within the range of 20–40, it means a very high enrichment, indicative of a very strong pollution, and if (EF > 40), it means an extreme enrichment, indicative of an extreme pollution signal.

The pollution index (PI) and Pollution load index (PLI) ~~were~~ arealsoused to assess potentially toxic elemen~~heavy metal~~t pollution in the soil, sediments, and dust. The pollution index (PI) was defined by the following equation4:

PI = Cn /Bn ……………………………………..…………. equation 4

where Cn and Bn are the measured and background concentrations of metal n, respectively, in the surface sediment samples. PI is classified by Faiz,*et al.*[**23] (**as follows: PI ≤ 1 indicates a low level of pollution; 1< PI ≤ 3 indicates a middle level of pollution, and PI > 3 a high level of pollution. The pollution Load Index (PLI) for each sample was calculated following the method byTomlinson, *et al.* and Soares, *et al.* [**24 and 25].** It was defined by the following equation5:

$$\mathrm{PLI} = \sqrt[n]{\mathrm{CF1} + \mathrm{CF2} + \mathrm{CF3} + \cdots + \mathrm{CFn}}$$ ……………….……………. equation5

Where; n is the number of metals (six in the present study) and CF is the contamination factor. The contamination factor (CF) can be calculated from the following relationstatedin equation 6:

~~is calculated from the following relationship in equation 6:~~

$$\mathrm{CF} = \frac{\text{(Cn)Concentration of the ~~heavy metal~~potentially toxic element in the soil sample}}{\text{(Bn)Background concentration of the same ~~metal~~element}}$$
……..………equation6

where Cn is the measured concentration of a ~~heavy metal~~potentially toxic element in the surface sediments, and Bn is the background value. According to~~,~~Faiz, *et al.*, Harikumar, *et al.* and Seshan, *et al.*[**23, 26 and 27]**, the PLI value (PLI ≤ 1) indicates a low level of pollution, while 1< PLI ≤ 2 indicates a middle level of pollution and PLI >2 a high level pollution; while ~~. Where;~~the background value is in average shale [**21]**.

The gGeo-accumulation index (Igeo) was used by Muller and Wuana, *et al.*[**28 and 29]** ~~to~~ for the assessment ofpotentially toxic element ~~heavy metal~~ pollution. The Igeo was used to assess

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Formatted: Add space between paragraphs of the same style metal contamination in urban soils by comparing current and pre-industrial values **[29, 30]**. In this study, the geo-accumulation index (Igeo) was used to determine the extent of potentially toxic element~~heavy metal~~ pollution study of~~in~~ Wadi Al-Wala surface sediments. The Igeo was calculated using the following equation~~s are used in the calculation by equation~~7 [**31**]:

$$Igeo = \log_2 (Cn/1.5Bn) \quad \text{……………………………..………equation7}$$

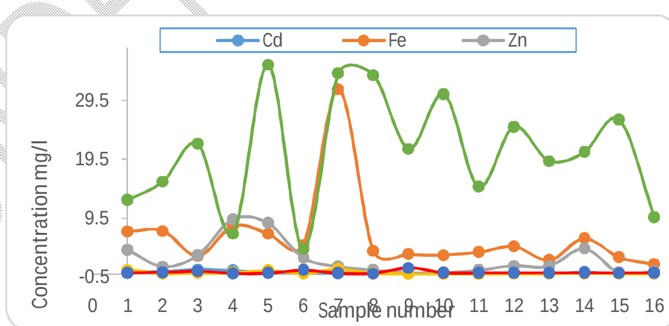
Where Cn is the concentration of the element 'n', and Bn is the geochemical background value of the element n, and 1.5 is the background matrix correction factor due to lithogenic effects. The geochemical background value in average shale is used to calculate Igeo [**21**]. The geo-accumulation index (Igeo) scale consists of seven grades from 0 to 6, ranging from unpolluted to highly polluted [**31, 32**]. The ~~G~~geo-accumulation index value class designation of sediment quality is as follows:

Igeo< 0 unpolluted environments
0 <Igeo ≤ 1 unpolluted-to-moderately polluted
1 <Igeo ≤ 2 moderately polluted
2 <Igeo~~.~~ ≤ 3 moderately-to-strongly polluted
3 <Igeo ≤ 4 strongly polluted
4 <Igeo ≤ 5 strongly to- extremely- polluted, and
Igeo >5 extremely polluted

5. Result and Discussion

~~5.1~~ 5.1 ~~Heavy Metal~~Potentially Toxic Element Distribution

The chemical concentrations of the ~~heavy~~ potentially toxic elements~~metals determined~~ in the surface samples from~~for~~ the study ~~sample~~ area are ~~listed~~ presented in Table 1. The variable concentration of the potentially toxic element~~heavy metal~~ distributions ~~along~~ in~~Wadi Al Wala~~ Wadi Al-Wala area ~~has~~ are shown in Fig. 4. ~~The high level of~~ Cu, Mn, Pb, Cd, Cr and Ni were observed to have high concentration levels in ~~was found along the Wadi Al-Wala~~ the study area. CaO in wt.% and percentage of organic matter (OM%) for surface sediment samples from Wadi Al-Wala area are given in Fig.4.



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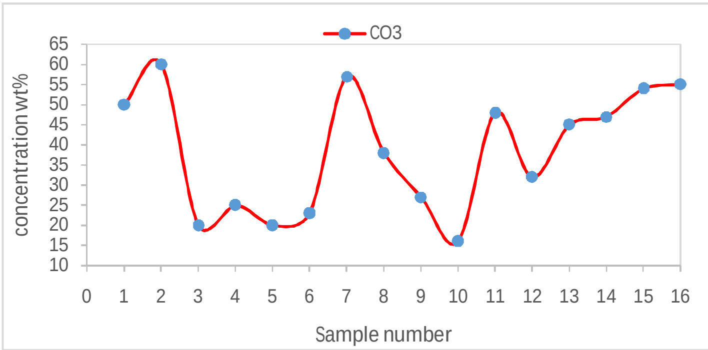

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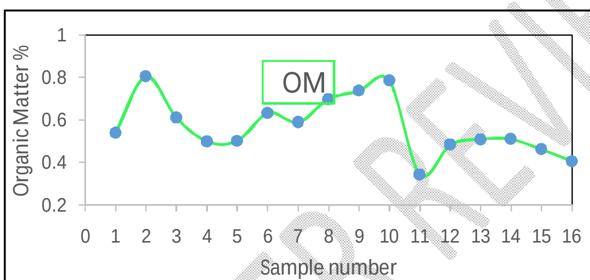

(C)

Fig.~~:~~4:(A):Distribution of metal concentration (ppm) for Cd, Fe, Zn, Cu, Pb, and Mn and (B):CaO wt% and (C): percentage of organic matter (OM%) ~~and CaO wt%~~ for ~~the~~ surface~~s~~ sediment samples from Wadi Al-Wala area

~~5.1.1~~ 5.1.1Statistical Analysis

The statistical correlation analysis ~~can be~~is used ~~as a way~~to indicate correlation between ~~any~~ two variables andto indicate the strength of relationship between ~~these variables~~them. Table 2shows the correlation matrix ofpotentiallytoxic elementsin the samples from the study area. High correlation between Fe with Cu (r = 0.74) and Cd with Zn (r = 0.59), Cu with Zn (r= 0.41)(Table 2), ~~these result to the~~ are indicative of theirsimilar ~~same~~main sources~~ of this metals~~.

Table 2: Correlation m~~M~~atrix ~~for~~ of~~the Heavy Metals~~potentially toxic elements fromstudy area ~~of the Studied Samples~~

	Cd	Fe	Zn	Cu	Pb	Mn
Cd	1.000					
Fe	-0.015	1.000				
Zn	0.590	0.098	1.000			

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Cu	0.194	0.741	0.414	1.000		
Pb	-0.095	-0.191	-0.237	-0.288	1.000	
Mn	-0.241	0.302	-0.137	0.268	-0.231	1.000

5.1.2 Enrichment Factor (EF)

The resultss of EF in Table 3, indicate that high concentrations of Zn and Cd are present in the analyzed samples (Fig. 5). This may result with riskyere is environmental risk of Zn and Cd pollution in Zn and Cd considering that the study areabecauseof their EF -thevalue for extreme pollution according to EF is>40indicative of extremepollution level. These heavy metals can be derived from anthropogenic source, such as; fertilizers and pesticides used in agricultural activities. The fluctuation in EF values can be accredited to the changes in the amount of contribution for each metal in the sediments or to the variance in the removal rate of each metal from the sediments. The high percent of the EF for Cd and Zn in the samples 3, 4 and 5 reflections pointto the main sources of contamination being from in the along the stream for the agricultural activitiesy in these study area [32].

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Table 3: Enrichment Factor (EF) of potentially toxic elements from study area

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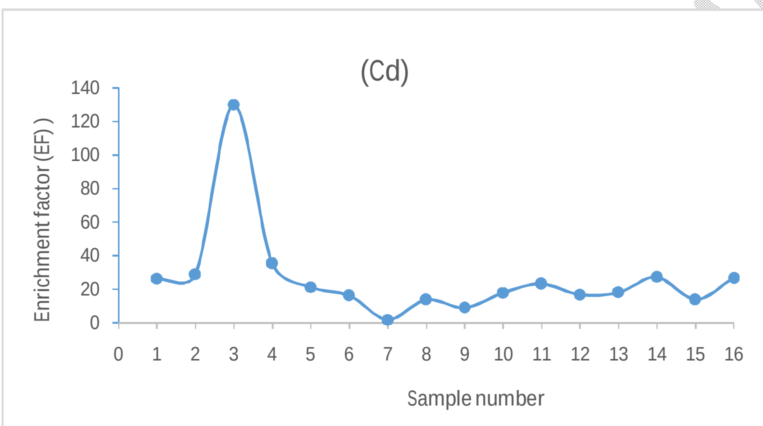
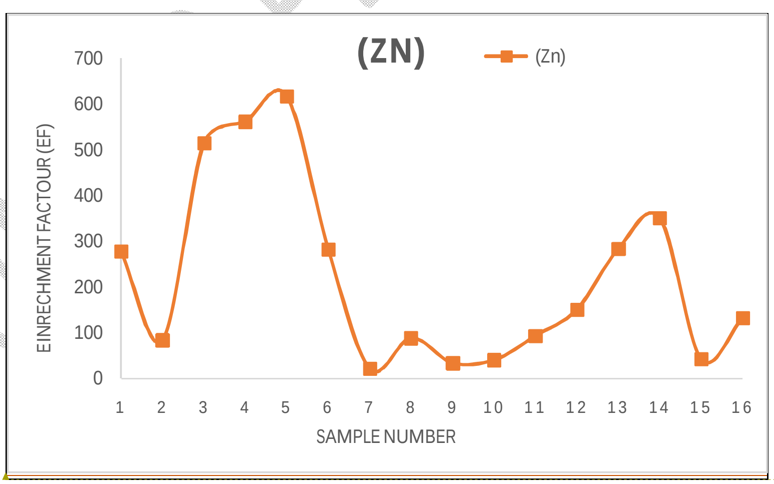
	Enrichment Factor (EF)				
Sample	(Cd)	(Zn)	(Cu)	(Pb)	(Mn)
1	26.52	277.43	0.19	0.07	9.89
2	28.88	83.47	0.02	0.09	12.22
3	130.10	514.79	0.13	0.35	41.35
4	35.46	562.12	56	0.04	4.83
5	21.36	617.57	0.16	0.05	29.38
6	16.34	282.63	0.03	0.34	5.05
7	1.93	20.47	0.05	0.01	6.17
8	13.90	87.88	0.06	0.09	49.50
9	9.01	33.25	0.01	0.76	35.87
10	18.02	39.79	0.02	0.15	53.44
11	23.25	92.36	0.03	0.13	22.74
12	16.75	150.51	0.03	0.10	30.23
13	18.12	283.16	0.06	0.21	46.91
14	27.31	350.34	0.04	0.08	19.46

15	14.05	41.40	0.05	0.19	52.46
16	26.74	131.33	0.08	0.29	33.37
Maximum	130.10	617.57	56	0.76	53.44
Minimum	1.93	20.47	0.01	0.01	4.83
Average	26.73	223.03	3.56	0.18	28.30



(A)



(B)

Fig. 5: The Enrichment Factor (EF) distribution for (A):Cd and (B): Zn in the studyarea

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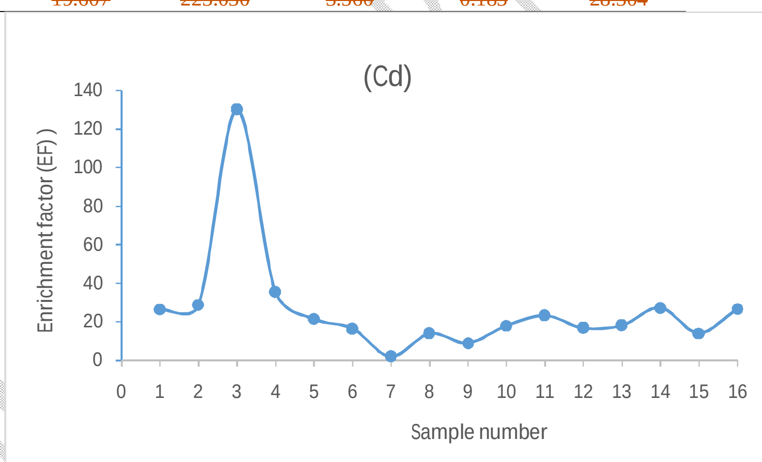
Table 3: Enrichment Factor (EF) of the heavy metal samples study

	Enrichment Factor (EF)				
Sample	(Cd)	(Zn)	(Cu)	(Pb)	(Mn)
1	26.521	277.434	0.192	0.065	9.891
c2	28.884	83.468	0.022	0.093	12.218
3	130.101	514.788	0.129	0.352	41.345
4	35.458	562.115	56.000	0.037	4.831
5	21.358	617.568	0.159	0.051	29.381
6	16.338	282.626	0.034	0.338	5.053
7	1.925	20.470	0.051	0.012	6.169
8	13.902	87.879	0.060	0.086	49.502
9	9.008	33.250	0.013	0.756	35.872
10	18.023	39.794	0.024	0.150	53.435
11	23.250	92.356	0.029	0.125	22.741
12	16.746	150.506	0.027	0.098	30.232
13	18.122	283.158	0.060	0.211	46.912
14	27.312	350.341	0.035	0.079	19.460
15	14.045	41.396	0.051	0.188	52.459
16	26.743	131.326	0.083	0.293	33.370
Maximum	12.604	617.568	56.000	0.756	53.435
Minimum	18.484	20.470	0.013	0.012	4.831
Average	19.607	223.030	3.560	0.183	28.304



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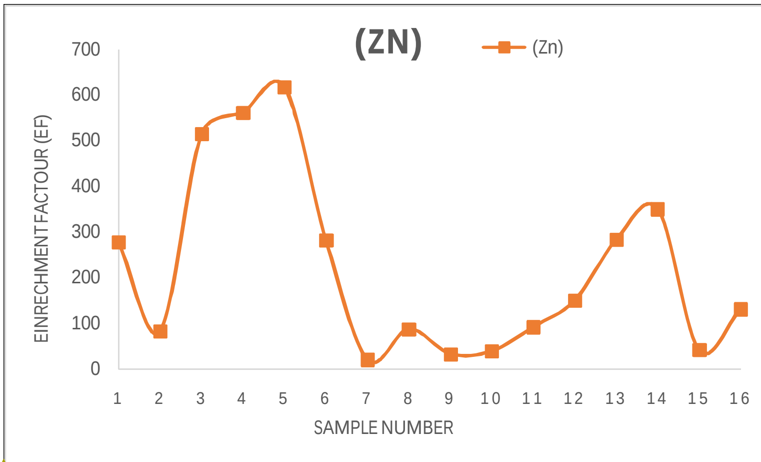

Fig. 5: The Enrichment Factor (EF) distribution for Cd and Zn of the study samples

5.1.3 Geo-accumulation Index (Igeo)

The Igeo result and distribution in the study samples areaare shows presentedin Table 4 and Fig. 6. The percent of Igeo differ according to the type of metal and its location. Fe, Pb and Cu remain in grade < 0 (unpolluted) in all stations suggesting that the study area sediments are in background value with respect to this metal. While, Mn, Zn and Cd are in the range of moderately to strongly polluted; depending on the location of the sample and the contributors in elementals concentrations. The highest Igeo grade was attributed to Zn as it exceeds 5 in some places showing that the sediment samples are extremely polluted. The concentrations of Fe, Pband Cu are within safe level and that they weredetectedto be practically unchanged by anthropogenic influences, unlike like Zn, Cdand Mn which exceeded their average concentration values.This suggests that the sediments of Wadi Al Wala are having background concentrations for Mn, Cd, and Zn; these elements are practically unchanged by anthropogenic influences.Besides agricultural sources, Zn, Cd and Mnin the study areamay have been These dangerous metals can bederived from industrial waste and gasoline additives used in industries and automobiles [**33, 34**]. In addition, they might be derived from corrosion agricultural activities in the Wadi.

Table 4: The Igeo values of the heavy metal forpotentially toxic elements from the study samplesarea.

Geo-accumulation Index (Igo)						
sample	Cd	Zn	Cu	Pb	Fe	Mn
1	1.46	4.84	-5.66	-7.21	-3.27	0.03
2	1.60	3.13	-8.75	-6.69	-3.25	0.36
3	2.50	4.49	-7.47	-6.03	-4.52	0.85

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4	2.04	6.03	-7.27	-7.88	-3.10	-0.83
5	1.08	5.93	-6.00	-7.62	-3.34	1.54
6	0.18	4.29	-8.72	-5.42	-3.85	-1.51
7	-0.21	3.20	-5.46	-7.48	-1.15	1.47
8	-0.37	2.29	-8.24	-7.70	-4.17	1.46
9	-1.2	0.68	-10.67	-4.77	-4.37	0.79
10	-0.25	0.89	-9.80	-7.17	-4.43	1.31
11	0.30	2.29	-9.36	-7.24	-4.24	0.27
12	0.17	3.34	-9.13	-7.24	-3.89	1.03
13	-0.73	3.24	-8.97	-7.15	-4.91	0.65
14	1.24	4.92	-8.37	-7.19	-3.53	0.75
15	-0.81	0.75	-8.91	-7.03	-4.62	1.09
16	-0.67	1.63	-9.00	-7.18	-5.41	-0.35
maximum	2.50	6.03	-5.46	-4.77	-1.15	1.54
Minimum	-1.2	0.68	-10.67	-7.88	-5.41	-1.51
Average	0.4	3.25	-8.24	-6.94	-3.88	0.56

Geoaccumulation Index (Igo)

sample	Cd	Zn	Cu	Pb	Fe	Mn
1	1.457	4.844	-5.65544	-7.205	-3.272	0.034
2	1.600	3.131	-8.75166	-6.687	-3.253	0.358
3	2.502	4.486	-7.4735	-6.029	-4.522	0.848
4	2.044	6.031	-7.26683	-7.878	-3.104	-0.832
5	1.075	5.929	-5.99739	-7.623	-3.342	1.535
6	0.180	4.292	-8.71887	-5.416	-3.850	-1.513
7	-0.209	3.202	-5.45651	-7.480	-1.154	1.471
8	-0.373	2.287	-8.24041	-7.703	-4.170	1.459
9	-1.200	0.684	-10.671	-4.774	-4.371	0.794
10	-0.254	0.889	-9.80229	-7.165	-4.425	1.314
11	0.304	2.294	-9.36171	-7.236	-4.235	0.272
12	0.174	3.342	-9.12851	-7.243	-3.892	1.026
13	-0.727	3.239	-8.96578	-7.152	-4.907	0.645
14	1.243	4.924	-8.37442	-7.193	-3.529	0.754
15	-0.807	0.752	-8.9092	-7.033	-4.619	1.094
16	-0.667	1.629	-9.00478	-7.179	-5.408	-0.347

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~~maximum~~	~~2.502~~	~~6.031~~	~~-5.457~~	~~-4.774~~	~~-1.154~~	~~1.535~~
~~Minimum~~	~~-1.200~~	~~0.684~~	~~-10.671~~	~~-7.878~~	~~-5.408~~	~~-1.513~~
~~Average~~	~~0.820~~	~~3.247~~	~~-8.236~~	~~-6.937~~	~~-3.878~~	~~0.557~~

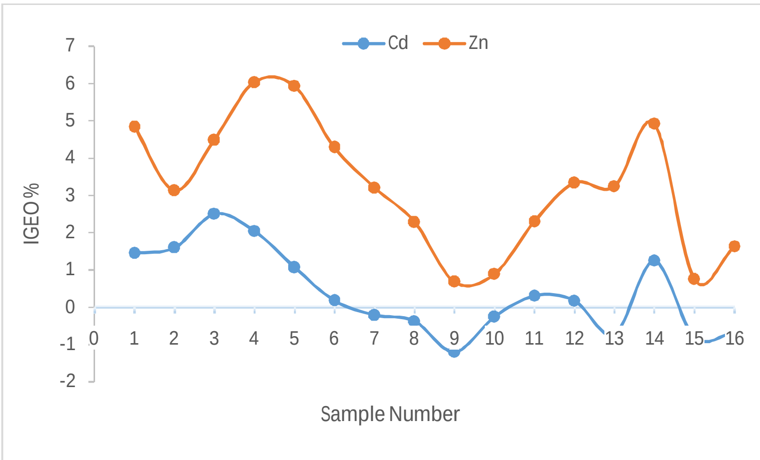

Figure 6:The Igeo v~~V~~alues d~~D~~istrbution ~~for~~ of potentially toxic elementsin the study area~~the Heavy Metals for the Studied Samples~~

5.1.4 Pollution Load Index (PLI)

Pollution severity and disparity in the study area were determined by applying pollution load index method. This index is a tool to compare the pollution grade in different places [**35**]. The contamination factor (CF) can be calculated from the following relation:

(CF) = Metal concentration in the sediments/Background value of the metal;~~ (6) number of toxic metal for the samples study. Where;~~ where background value is in average shale [**21**].

The PLI value of> 1 is polluted, whereas, < 1 indicates no pollution [**26**].

~~The study results in~~ Table 5shows the ~~, indicate that~~ CF values of the six potentially toxic elements. ~~all metals such as~~ Fe, Cu, and Pb ~~are~~ have low CFvalue~~low (~~<1~~)~~. That indicates that Fe, Cu and Pbhaveno pollution riskin the study area.On the other, hand, Zn, Cd andMnhave CFor PLI >1. The result shows that the study areaishighlypolluted withZn, Cd andMn. ThePLI~~Indices~~fluctuations in valuesare the ~~is a result of~~ various indices' sensitivity towards sediment pollutants [**36, 37**]. ~~PLI results indicate that there are no pollution threats in the study area as low indices reported [37].~~

Table 5: PLI values (CF) of ~~the heavy metal for~~potentiallytoxic elementsinthe study ~~samples~~area~~.~~

Sample No.	Cd	Fe	Zn	Cu	Pb	Mn	Pl
1	4.117	0.155	43.071	0.030	0.010	1.536	0.012789
2	4.546	0.157	13.137	0.003	0.015	1.923	0.000916
3	8.497	0.065	33.621	0.008	0.023	2.700	0.009765

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4	6.186	0.174	98.063	0.010	0.006	0.843	0.005538
5	3.160	0.148	91.379	0.023	0.008	4.347	0.033192
6	1.699	0.104	29.389	0.004	0.035	0.525	0.000341
7	1.298	0.674	13.800	0.034	0.008	4.159	0.014411
8	1.158	0.083	7.321	0.005	0.007	4.124	0.000104
9	0.653	0.072	2.411	0.001	0.055	2.601	0.000015
10	1.258	0.070	2.778	0.002	0.010	3.730	0.000016
11	1.852	0.080	7.357	0.002	0.010	1.811	0.000045
12	1.692	0.101	15.205	0.003	0.010	3.054	0.000211
13	0.906	0.050	14.158	0.003	0.011	2.346	0.000048
14	3.550	0.130	45.537	0.005	0.010	2.529	0.002462
15	0.857	0.061	2.526	0.003	0.011	3.201	0.000015
16	0.945	0.035	4.640	0.003	0.010	1.179	0.000006
maximum	8.497	0.674	98.063	0.034	0.055	4.347	0.033192
Minimum	0.653	0.035	2.411	0.001	0.006	0.525	0.000006
average	2.648	0.135	26.525	0.009	0.015	2.538	0.004992

6. Conclusions and Recommendations

Wadi Al-Wala sediments contamination assessment was carried out using the pollution indicators,; namely: enrichment factor (EF), geo-accumulation index (Igeo),andpollution load index (PLI), and geo accumulation index (Igeo).. The percentage of organic matterand carbonate inweight percentagewerealso assessed for the surface sediments from the study area.ThecCorrelation coefficients analysis of concentrations the potentially toxic elementswas carried out to establish the elemental relationships and to decipher their among TOM, CO, Cu, Zn, Cd, Mn, Fe, and Pb was also applied showing that there are varying correlations among them indicating complex geochemical behaviors. The following conclusion for the study result:

In this study,the followingfindings have been established:

- The Igeo analyses of Wadi Al-Wala sediments proved that the concentrations of MnFe, Cu, and Pb,and Fe are within safe levelsand that these elements are werepractically unchanged by anthropogenic influences. Conversely, ,whilethe concentrations of Zn,and Cd and Mnexceeded the average valuesand they pose serious environmental pollution risk min the studyarea. The elevated concentrations of Cd and Zn,Cd and Mn may be attributedcan be due to anthropogenic sources, such as phosphate fertilizers,andand pesticides used uses in agricultural lands and industrial waste and gasoline additives used in industries and automobilesin the Wadi Al-Walaand agricultural use of sewage sludge and seepage of domestic wastewater from cesspits in nearby villages to the Wadi and natural weathering of surrounding geological formations. .
- The PLI analysis proved confirmed that Wadi Al-Wala is aleadyheavy polluted with Zn, Dc and Mn.

moving towards a probable environmental pollution with regard to heavy metals (Zn and Cd) if experts did not control these external sources.

- EF assessement corroborated theresult for showed high concentrations ofZn, Cu Cdand Cd Mnin the study area; thehigh concentrations of these potentiallytoxic elements have been inferred to anthropogenic sources.

Cd increased in some samples due the use of cadmium containing raw phosphate to prepare fertilizers which used on the frames within studied area and watering of livestock at the Wadi and seepage of domestic wastewater from cesspits in nearby villages to the Wadi and alzibar put material up through the valleys and the increasing number of farmers in the Wadi Al -Wala and the use of organic materials .

- The current study has established ~~confirmed~~ that long-term use of phosphate fertilizer that contains a high level of Cd may lead to accumulation of Cd in the soil, and this may eventually increase plant Cd uptake and into thefood chain[**29**].
- The soil characteristics~~,~~ such as c~~C~~lay content of the soil, organic matter and calcium carbonate and degrees of salinity and acidity may alsoplaysome ~~with a~~ key roleswith respect to~~on the content~~the Cdconcentrationsin soils in the study area~~of the soil from cadmium~~ [**38, 39**].
- Regularenvironmental pollution monitoringand mitigation inclusive of management and control of anthropogenic dischargesare recommended for Wadi Al-Wala area.
-
- ~~Natural weathering of surrounding rock formations can act as another source of heavy metals in the sediments, increase the proportion of lime in the soil with a high temperature help to increase the adsorption cadmium in calcareous soils [**39**].~~
- ~~The chief pollution sources of Zn and Cu in some samples are agricultural use of sewage sludge and the use of agro-chemicals such as phosphate fertilizers and pesticides, Furthermore. The proliferation of septic tanks in residential communities bordering put him in addition to its cargo tanks seepage in the neighboring valleys.~~
- ~~The variation of Mn concentration in the study area was due to irrigation of land by industrial wastewater and other agronomic practices and high value of organic matter. The major anthropogenic sources of Mn include municipal wastewater discharges, sewage sludge, industries in the jiza area oil shale mines and processing plants.~~

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